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(71) Applicant: INNOTECH, INC. [US/US]; 5568 Airport Road, Roanoke, VA 24012 (US).

(72) Inventors: GUPTA, Amitava; 5312 Hampden Lane, Bethesda, MD 20814 (US). BLUM, Ronald, D.; 5320 Silver Fox Road, Roanoke, VA 24014 (US). IYER, Venkatramani, S.; 152 Summit Way, Roanoke, VA 24014 (US).

(74) Agents: WELLS, William, K., Jr. et al.; Kenyon & Kenyon, 1025 Connecticut Avenue, N.W., Washington, DC 20036 (US).

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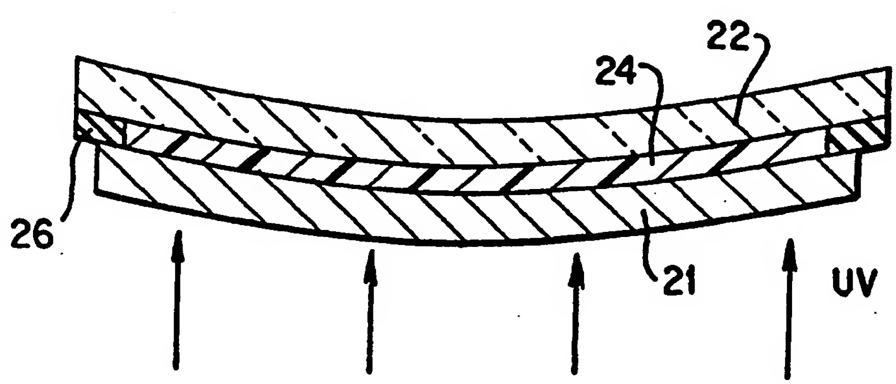

(57) Abstract

Adhesive matrix layers (24) and sublayers and methods for their preparation are described. The adhesive matrix layers (24) and sublayers provide effective reservoirs for photochromic additives and can serve as an effective transition region between dissimilar materials to be used in optical articles which transmit or refract light.

ADHESIVE PHOTOCHROMIC MATRIX LAYERS FOR USE IN OPTICAL ARTICLES

FIELD OF THE INVENTION

This invention relates to adhesive matrix layers that provide effective reservoirs for photochromic additives and can serve as an effective transition regions between dissimilar materials to be used in optical articles which transmit or refract light.

BACKGROUND

Surfaces of optical articles may be treated or altered for many reasons. For example, it is desirable in some instances to coat a lens with an outer layer, such as a hard, scratch-resistant layer or an anti-reflective layer, to improve the wear or optical characteristics of the finished lens. In other instances, a tintable hard coat is provided over a soft polycarbonate material. In still other instances, the lens optic is tinted with a heat diffusion process, either with or without the application of a hard coat.

At the same time, it is often desirable to pretreat the surface of an optic prior to application of an outer

layer to promote strong adhesion between the surface of the optic and the outer layer. Such pretreatments include the use of specialized cleaning or etching processes or the application of surface primers. In general, the pretreatment should not adversely affect the quality of the optic, nor should it add substantial thickness to the optic. An example of such pretreatments may be found in U.S. Patent No. 5,316,702 to Blum, Gupta and Bennington. Unless indicated to the contrary, all references cited herein are incorporated by reference in their entireties.

While effective surface treatment processes are known in the art, such processes nonetheless have room for improvement. For example, prior art surface pretreatments do not provide effective and efficient reservoirs for various additives, such as photochromic additives. Nor do they effectively serve as transition regions between dissimilar materials.

SUMMARY OF THE INVENTION

In view of the above deficiencies of the prior art, it is an object of the present invention to provide an adhesive matrix layer between an optical substrate and an outer barrier layer, that will act as an effective reservoir for various additives.

It is another object of the present invention to provide an adhesive matrix layer that will act as a transition region between an optical substrate and an outer barrier layer made from dissimilar materials.

It is yet another object to the present invention to provide a process for creating such an adhesive matrix layer. These and other objects are met by the present invention, which relates to discrete adhesive matrix layers and to methods for fabricating the same. The adhesive matrix layers of the present invention have several advantages over the prior art.

A first advantage of the present invention is that it provides novel adhesive matrix layers that serve as spacer layers between a substrate surface and an outer barrier layer, allowing bonding of two materials with dissimilar cross link densities and hardnesses.

A second advantage of the present invention is that it provides novel adhesive matrix layers that serve as repositories for additives, such as UV absorbers, colored materials for development of lens tint, photochromic additives and so forth. Losses of these additives from the adhesive matrix layers of the present invention through diffusion are significantly reduced, since both sides of the adhesive matrix layer are generally covered by layers that are resistant to diffusion.

According to an embodiment of the present invention, an optical product is provided comprising an adhesive matrix layer attached to an optical substrate and having a thickness of greater than 25 μm.

According to another embodiment, an optical product is provided that comprises an adhesive photochromic matrix layer attached to an optical substrate. An outer barrier layer is attached to the adhesive photochromic matrix layer. The outer barrier layer in this embodiment is attached without the use of an additional adhesive.

According to another embodiment, an adhesive matrix layer is provided that has a thickness of greater than 25 μm. The adhesive matrix layer in this embodiment is adapted to act as a reservoir for one or more photochromic additives and as a transition region between dissimilar materials. The adhesive matrix layer in this embodiment preferably has one or more characteristics selected from the group consisting of a cross link density that is less than that of commercially available CR-39 lenses and a Tg between 10 and 60 °C.

According to yet another embodiment, a method is described wherein an adhesive matrix layer is provided on an optical substrate. The adhesive matrix layer in this embodiment has a thickness greater than 25 μm on at least one surface of the optical substrate.

According to another embodiment, a mold is coated with a resin corresponding to the adhesive matrix layer, forming a coated mold. Then, an accessory mold and a substrate resin are provided which are arranged, along with the coated mold, such that the space between the coated mold and the accessory mold is filled with the substrate resin and such that the volume occupied by the substrate resin corresponds to the shape of the optical substrate. The substrate resin is cured, and the adhesive matrix layer is transferred to the substrate, since it has a greater affinity for the substrate than for the mold. If desired, a photochromic additive can be included in the uncured adhesive matrix layer resin. Alternatively, a photochromic layer can be placed on the mold prior to coating the mold with the resin corresponding to the adhesive matrix layer. As a additional alternative, a hard coat material can be placed on the mold, followed by a photochromic layer, prior to coating the mold with a resin corresponding to the adhesive matrix layer.

According to another embodiment, a resin corresponding to the adhesive matrix layer is provided on at least one surface of the optical substrate, and the resin is cured to form the adhesive matrix layer, which is later imbibed with a photochromic additive.

According to another embodiment, a method for the manufacture of an optical substrate having an attached adhesive matrix layer is provided. The method comprises: (a) providing an optical substrate; (b) providing a first adhesive matrix sublayer on at least one surface of the optical substrate; and (c) providing a second adhesive matrix sublayer on the first adhesive

matrix sublayer to provide a network of adhesive matrix sublayers.

The above adhesive matrix layers and sublayers are preferably provided with one or more photochromic additives.

Other objects and advantages of the invention and alternative embodiments will readily become apparent to those skilled in the art, particularly after reading the detailed description, and examples set forth below.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows a sectional view of an optical substrate, an adhesive matrix layer, and an outer barrier layer.

Figure 2A shows a mold assembly used to form the adhesive matrix layer.

Figure 2B shows a side view of a mold assembly under ultraviolet irradiation.

Figure 3 shows a lens with an adhesive matrix layer that is mounted on a block for spinning at high speed.

Figure 4 shows the side view of a mold assembly set up to form an outer barrier layer over the adhesive matrix layer.

Figure 5 shows a mold assembly under ultraviolet irradiation.

DETAILED DESCRIPTION OF THE INVENTION

According to an embodiment of the present invention, an adhesive matrix layer is provided on the surface of an optical substrate. As used herein, the term "optical substrate" is used to designate an article that is either currently capable of transmitting or refracting light, or will be able to do so when finished. Such optical substrates include optical preforms, optical wafers, optical lenses, semi-finished lens blanks, windows and the like. Typical materials

for use as optical substrates include, without limitation, bisallyl carbonate (CR-39), polymethyl methacrylate and polycarbonate of bisphenol A.

The adhesive matrix layer (which for purposes of the present invention is either a single layer or an accumulation of multiple layers) is preferably strongly bonded to the surface of the optical substrate, has optical properties consistent with the optical function of the optical substrate, and is resistant to erosion by solvents. The adhesive matrix layer of the present invention can serve many functions, including the development of a strong and durable bond between the optical preform below it and the outer barrier layer above it, and the ability to serve as a reservoir for various additives.

In general, the adhesive matrix layers of the present invention preferably satisfy several physical and optical criteria.

For example, the layer is substantially transparent to radiation which the lens or the lens blank is meant to refract or transmit. Thus, if the lens is meant to focus or defocus visible light (i.e, light having a wavelength of about 400-700 nm), then the adhesive matrix layer should be as optically clear as possible in this wavelength region. Moreover, the adhesive matrix layer of the present invention preferably has a refractive index that is matched to that of the optical substrate. Preferably, the refractive index of optical substrate is not more than 0.05 units, and more preferably not more than 0.03 units, different from the refractive index of the adhesive matrix layer.

The glass transition temperature (T_g) of the adhesive matrix layer affects several properties of the adhesive matrix layer. For example, an increase in glass transition temperature results in the following: (1) a decrease in the permeability of the adhesive matrix layer at a given temperature (because the

adhesive matrix layer becomes more permeable to additives at temperatures above the glass transition temperature), (2) a higher tensile or bulk modulus of the adhesive matrix layer at a given temperature (because the modulus of the adhesive matrix layer becomes harder at temperatures below the glass transition temperature), (3) slower switching time of any photochromic additives, (4) higher dynamic range of any photochromic additives and (5) higher resistance to photochemical damage.

The glass transition temperature is typically controlled by changing the resin composition. For example, if two resins are combined, with the first resin having a higher T_g than the second resin, then the T_g of the blend can be increased by increasing the relative amount of the first resin.

The cross link density also affects several properties of the adhesive matrix layer. For example, an increase in cross link density results in the following: (1) an increase in the rigidity of the layer (and thus a decrease in impact strength) at temperatures above the glass transition temperature, (2) a decrease in the permeability of the layer to additives (because the layer is resistant to swelling by common organic solvents such as acetone or hexane), (3) a decrease in the switching time of any photochromic additives, and (4) an increase in the dynamic range of any photochromic additives.

The cross link density is typically controlled by controlling the degree of functionality of the resin components. For example, monomers with a greater number of reactive functional groups generally result in polymers with greater cross link density.

In view of the above, it can be seen that the glass transition temperature can be optimized for a given end application, based on a trade-off between dynamic range and resistance to photochemical damage v. permeability

and impact strength at a given temperature, as well as switching speed. At the same time, the cross link density can be optimized for a given end application, based on a trade-off of matrix permeability, impact strength and switching time v. dynamic range.

Preferably, the glass transition temperature and the cross link density of the adhesive matrix layer are simultaneously optimized, since both have an affect upon properties such as the switching speed and dynamic range of photochromic additives, as well as impact strength and permeability of the layer to additives. In general, the adhesive matrix layer is preferably selected to have a low cross link density to provide good shear strength, fast switching and increased uptake of photochromic additives. In particular, the adhesive matrix preferably has a cross link density that is less than that of commercially available CR-39 lenses, more preferably less than about 3 mols/l and most preferably less than about 2 mols/l. At the same time, the adhesive matrix layer is preferably selected to have a glass transition temperature close to the service temperature of the finished product. For ophthalmic lens applications, the glass transition temperature of the adhesive matrix layer is preferably between 10°C and 60°C, and more preferably between 20°C and 40°C. This provides a reasonable degree of resistance to photochemical damage and dynamic range, without significantly deteriorating the matrix permeability and strength, as well as the switching speed of any photochromic additives.

In order to satisfy the above criteria, the adhesive matrix layer is preferably formulated from a mixture of monomeric and oligomeric acrylates, methacrylates, allyl or vinyl derivatives such as bisallyl carbonate or styrene. While optional, the formulation also preferably includes a thermal polymerization initiator (such as benzoyl peroxide,

2,2'-azoisobutyronitrile, or diisopropyl peroxydicarbonate), a photoinitiator (including derivatives of acetophenone and benzophenone such as 2-hydroxy-2-methyl-1-phenyl-propan-1-one or 1-hydroxycyclohexylphenyl ketone, sold by Ciba Geigy as Irgacure 184 and Durcure 1173), or both, depending on whether the resin is cured thermally, photochemically or both.

In other applications, it may be desirable to enhance the diffusivity of the additives in the adhesive matrix layer. In addition to conventional methods involving heat, aging, vibration, ultraviolet radiation and infrared radiation, it is also possible to enhance diffusivity by only partially curing the adhesive matrix layer prior to the diffusion of additives. After diffusion, the cure of the adhesive matrix layer is completed to increase the degree of cross linking.

The adhesive matrix layer is preferably strongly bonded to the optical substrate. To develop good bonding between the adhesive matrix layer and the lens or the lens blank, methods described in U.S. Patent No. 5,316,702 may be used.

The adhesive matrix layer of the present invention can be provided on any surface of the optical substrate. For example, in the case where the optical substrate is a lens that is adapted to provide distance correction, the adhesive matrix layer can be provided on the anterior (convex) surface of the optical substrate, the posterior (concave) surface of the optical substrate, or both. The adhesive matrix layer is provided on the anterior (convex) surface for most applications.

The cumulative adhesive matrix layer of the present invention is also preferably provided in either a combined or a single thickness of greater than 25 μm, more preferably from 100 to 250 μm. In the event multiple sublayers are used to form a cumulative layer, such sublayers are appropriately dimensioned to provide

the proper cumulative dimension. For example, three layers of about 30 to 80 μm can be used, ten layers of about 10 to 25 μm can be used and so forth.

Hard-coat layers that are commonly applied to the surfaces of optical substrates have many properties that differ significantly from those of the adhesive matrix layers of the present invention. For example, such hard-coat layers have thicknesses generally under 25 μm, have high cross link densities, have T_g's greater than about 75°C, and they have the inability to adhere and strongly bond to adjacent layers once the hard-coat layer is cured. In contrast, the adhesive matrix layers of the present invention preferably have thicknesses of more than 25 μm, have low cross link densities, have T_g's between about 10 and 60 °C, and they have the ability to adhere and strongly bond to adjacent layers, even after the adhesive matrix layer is cured.

The adhesive matrix layers of the present invention can be created by numerous methods.

According to some embodiments of the present invention, the adhesive matrix layers are formed prior to or concurrently with the formation of the optical substrate. For example, the surface of a mold can be coated with an uncured adhesive matrix resin that is used to ultimately form the adhesive matrix layer. The coated mold can then be subjected to a partial cure, although both a complete cure and the absence of a cure are also contemplated. The coated mold can then be used in the formation of the optical substrate. For example, by including the coated mold in a conventional mold assembly that also comprises an accessory mold and a gasket, the space between the coated mold and the accessory mold can be filled with a substrate resin to provide an uncured resin mass that corresponds to the shape of the optical substrate. The entire assembly can then be cured to provide an optical substrate having an adhesive matrix layer. It is noted that the cured

adhesive matrix resin should have a greater affinity for the cured substrate resin, than for the mold.

In other embodiments, the adhesive matrix layers are provided on a pre-existing optical substrate, either by casting using a mold, or by fabricating the layer without a mold by spraying, by dip coating, by brushing, by flow coating, by spin coating, by curing the resin *in situ* in a resin bath, by photolithography and so forth. In such embodiments, the surface of the optical substrate may be pretreated before casting the adhesive matrix layer on it. Techniques for pretreatment can be found, for example, in U.S. Patent No. 5,316,702.

An example wherein the adhesive matrix layer is provided, using a mold, on a pre-existing optical substrate (i.e., a semi-finished lens blank) is illustrated in Figures 2A and 2B. In Figures 2A and 2B, a mold assembly set up to form the adhesive matrix layer is shown. In this particular mold assembly, the mold (21) is made of glass or other material transparent to radiation in the wavelength range of 300 - 400 nm. The mold (21) also has a curvature that is matched to the front curvature of the lens (23) or the semi-finished lens blank (22). The space between the mold (21) and the lens (23) or lens blank (22) is filled with a polymerizable resin layer (24). Figure 2B also shows the mold assembly under ultraviolet irradiation. The thickness of the resin layer is controlled in this example by flexible spacers (26) placed at three or more equidistant points along the circumference of the mold.

Of course, the adhesive matrix layer need not necessarily be created in a single step. For example, a first layer of adhesive matrix resin can be provided, and the adhesive matrix resin then cured, or partially cured, to form a first adhesive matrix sublayer. A second layer of adhesive matrix resin can then be provided on the first adhesive matrix sublayer and

cured, and so forth, until the correct added thickness is achieved.

The adhesive matrix layers or sublayers of the present invention may be provided with one or more desired additives, preferably photochromic additives. Photochromic additives are substances which display the characteristics of reversibly changing in color and/or degree of light transmission when they are exposed to some types of electromagnetic radiation, including sunlight, and turning back into their original color and/or transmission status when the electromagnetic radiation source is removed.

The substances endowed with photochromic characteristics known from the prior art are many, and belong to several classes of both inorganic and organic compounds, as described, e.g., in "Photochromism", G. H. Brown (Ed.), Vol. IV, from the Weisseberger Series "Techniques of Organic Chemistry", Wiley-Interscience, New York (1971). Among the preferred photochromic additives of the present invention are those compounds belonging to the class of the sprio-indoline-type compounds, which are capable of conferring photochromic characteristics to polymerized organic materials, such as those disclosed, e.g., in the following patents: U.S. Pat. Nos. 3,562,172; 3,578,602; 4,215,010; 4,342,668; EP 146 135, WO 85/02619; EP 245 020; and in European patent applications publ. Nos. 134,633 and 141,407. Such compounds include spiro(indolino) naphthoxazines, spiro(indolino) pyridobenzoxazines, spiro(benzindolino) naphthoxazines, spiro(benzindolino) pyridobenzoxazines, and so forth.

In the event that one or more photochromic additives are to be incorporated into the adhesive matrix layer, the absorption spectra of the photochromic additives are typically selected to give a grey, green, brown or blue appearance to the final product. It should be kept in mind that the switching rate of each

photochromic component is a function of the level of darkness, the temperature, and evolution of tint when being activated or deactivated, as well as the composition of the layer in which it resides.

A typical photochromic additive formulation contains a mixture of two or three photochromic additives, an antioxidant, such as 2,5-di(t-butyl) phenol, and an optional background tint (such as DIACOTE) to provide a cosmetically appealing tint. Such additive formulations also typically contain U.V. stabilizers known from the prior art, and capable of improving the duration of the photochromic effect, without impairing the intensity of photocolorability of the same mixtures. Nonlimiting examples of U.V. stabilizers for the purposes of the present invention are non-aromatic stabilizers such as hindered amines (HALS) and such as DABCO. The additive formulations can be prepared by grinding the individual components together, e.g., in a grinding mill, by dissolving them in a common solvent and evaporating the solvent, or by microencapsulating them with a layer of thermoplastic polymer.

A wide range of photochromic articles, which are capable of constituting an at least partial screen towards solar radiation in a reversible way, can be obtained by establishing one or more photochromic additives within the adhesive matrix layers of the present invention. Such photochromic articles include photochromic ophthalmic lenses and photochromic sun filters, such as lenses for sunglasses, prescription-lenses, contact lenses, glasses for cars or transport means in general, and windows in the building sector.

Several methods are available for establishing additives, particularly photochromic additives, within the adhesive matrix layers of the present invention. Such methods include those methods discussed in U.S. Patent No 5,180,524, and these methods are also suitable

for establishing suitable adjuvants for the photochromic additives (such as antioxidants, U.V. stabilizers, background tint, and so forth).

According to some embodiments, the desired additives are provided as part of the resin formulation used to create the adhesive matrix layer. According to other embodiments, the additives can be provided after the adhesive matrix layer is formed by impregnating the adhesive matrix layer by means of diffusion. Other embodiments envision a network of multiple adhesive matrix sublayers wherein the desired additive or additives are applied directly following the formation of each sublayer, or are applied once the desired number of adhesive matrix sublayers have been formed. Still other embodiments envision placing a layer of photochromic material on an optical substrate, and then placing an adhesive matrix layer (or layers) on the layer of photochromic material. The photochromic material can be optionally diffused into the adhesive matrix layer as follows.

Following incorporation of the additives, and preferably after the application of a hard coat or sealant, the additives are then dispersed/diffused throughout the sublayer by annealing, vibration, ultraviolet radiation, infrared radiation or aging with time. However, this dispersion/diffusion enhancement step can be performed at any time following the establishment of the adhesive matrix layer. One advantage to this multilayer approach is that very high loadings of additive can be achieved in the adhesive matrix layer. Another advantage of this multilayer approach is that one can customize, tune or balance the desired additive effect by applying the appropriate additive or additives in a layered manner.

The photochromic additive is applied to the surface of, or is incorporated into, the adhesive matrix layer

of the present invention by means of suitable techniques.

According to a first exemplary route, photochromic additives can be established into the adhesive matrix layer of the present invention by means of molding-based techniques wherein the photochromic additives are homogeneously dispersed throughout the adhesive matrix layer.

According to an alternative route, photochromic additives are dissolved in a suitable solvent, together with a suitable polymeric material, and the solvent solution is deposited on an optical substrate in order to form, after the evaporation of the solvent, a photochromic adhesive matrix layer.

According to another route, the photochromic additive is added to a suitable polymerizable monomer such that, after a polymerization is carried out in the presence of a suitable polymerization initiator, the photochromic additive is evenly incorporated into the adhesive matrix layer.

According to yet another route, the photochromic additive can be applied to the adhesive matrix layer by means of a surface impregnation, which is obtained by placing the adhesive matrix layer into contact with a solution or dispersion which contains the photochromic additive at a suitable temperature. For that purpose, a solution or suspension of the photochromic additive is prepared in a suitable solvent or dispersant, normally selected from among the usual organic solvents (e.g., acetone, hexane, tetrahydrofuran, methanol and acetonitrile, and so forth), silicone oils, fluorinated oils, and the like, and the photochromic compound is transferred on to the polymeric substrate by dipping the polymeric article in said solution or suspension, for suitable times and at suitable temperatures. Or the additive can be introduced by directly applying a solvent solution containing the additive onto the

adhesive matrix layer by means of brushing, dripping, spraying and so forth.

According to another route, the optical substrate with attached adhesive matrix portion can be mounted on a support that is capable of being rotated or spun at controlled speeds. Figure 3 shows a lens (31) with an adhesive matrix layer (32) mounted on a block (33) and placed on a support (34) capable of being spun at a high speed. The solution of the additive is added drop-wise on the surface of the lens as it is being spun on the support. Toric lenses or other optical substrates with non-centrosymmetric surfaces may require attachment to a block before they can be mounted on the support, to prevent them from wobbling upon being spun.

Other embodiments for loading the additive into the adhesive matrix layers of the present invention are discussed in connection with the Examples below. This in no way should be viewed to limit the processes of the present invention.

Once the desired adhesive matrix layer is achieved and loaded with an additive or additives, if any, the adhesive matrix layer is preferably overcoated with the outer barrier layer. Figure 1 shows a sectional view of an optical substrate (10) with an adhesive matrix layer (11), overcoated with an outer barrier layer (12).

The outer barrier layer of the present invention is preferably a sealing layer, acting as a barrier to the diffusion of the additives as well as oxygen. It may or may not be the outermost layer of the lens, but is simply "outer" as compared to the adhesive matrix layer.

The outer barrier layer may change the refractive power of the lens as a whole, it may result in a negligible change in the refractive power of the lens, or it may change the refractive power of the lens in part, as when providing an add power zone.

The outer barrier layer may be a hard coat layer such as those described in U.S. Patent No. 4,544,572,

the outer barrier layer may comprise a material like that used to form the optical substrate, preferably with a final hard coat layer, and so forth.

Depending on the specific application, the outer barrier layer may be cast either with the use of molds, or it may be cast without molds, for example, by curing *in situ* in a resin bath, dipping, spraying, brushing, flow coating or spin coating. Moreover, the outer barrier layer may be cast thermally, photochemically (as disclosed in U.S. Patent Nos. 5,178,800, 5,147,585 and 5,219,497) or both.

For example, a lens can be surfacecast (overcast) with an outer barrier layer that provides a desired add power correction. In this process, a mold is selected so as to provide the desired style and magnitude of the add power correction. The curvature of spherical portion of the mold preferably has a precise relationship relative to the curvature of the lens with the adhesive matrix layer, so as to attain a preselected final convex curvature after the casting process is completed. As above, if the cure of the resin involves application of ultraviolet radiation, the mold is preferably transparent to ultraviolet radiation in the appropriate wavelength range.

Figure 4 shows the side view of a mold assembly set up to form an overcoat or an outer barrier layer over the adhesive matrix layer. It consists of a lens (41) with an adhesive matrix layer (42) which is then placed on top of a resin (43) contained in a glass mold (44). The mold has a bifocal add power zone (441), with the remainder of the mold being a distance power zone (442). Figure 5 shows a mold assembly under ultraviolet irradiation, consisting of a semi-finished lens blank (51) with adhesive matrix layer (52), a resin (53) and a mold (54) whose curvature matches the curvature of the semi finished lens blank (51).

Other state of the art methods of overcoating may also be employed, such as those commonly employed to put on a scratch resistant layer on the surface of the lens.

The outer barrier layer may provide desirable optical properties, such as reduced reflection levels. The outer barrier layer may be designed to change surface hardness, scratch resistance, surface smoothness, or impact properties of the lens. Preferably, when incorporating photochromic additives in the adhesive matrix layer, the outer barrier layer is substantially a non-UV-blocking layer. By blocking as little UV radiation as possible, the photochromic additive activation is compromised as little as possible. The purpose of the outer barrier layer may be to provide an oxygen barrier and/or an acceptable level of surface hardness and/or reduced porosity, in order to minimize escape of additives loaded into the adhesive matrix layer and decrease the oxygen permeability. Such hard-coat layers preferably have a high cross-link density and a T_g of more than about 77°C.

The foregoing and following description of the invention and its various embodiments is not intended to be limiting of the invention but rather is illustrative thereof. Those skilled in the art can formulate further embodiments encompassed within the scope of the present invention.

EXAMPLES

Example 1

The following formulations are made up by mixing all ingredients in a flask, then stirring the mixture for 20 minutes at room temperature in the dark:

	PER CENT BY WEIGHT	
MONOMER/OLIGOMER	Lens 1	Lens 2
BIS ALLYL CARBONATE	60	5
ALKOXYLATED ALIPHATIC DIACRYLATE ESTER	18	22
TETRAHYDROFURFURYL ACRYLATE 1-HYDROXY	20	25
CYCLOHEXYLPHENYL KETONE	2	3

The experimental set-up employed is shown in Figure 2A. The resin in each case is placed as a thin layer in a mold assembly including: (1) a lens made of bisallyl carbonate (CR-39), having a surface that is modified as in U.S. Patent No. 5,316,702 and having a known convex radius; (2) a glass mold with a known concave radius which matches substantially the convex curvature of the lens; and (3) a resin as described in the table above, with the resin being placed as a thin layer between the lens and the mold. The thicknesses of the adhesive matrix layers are varied from 0.06 mm to 0.26 mm by affixing flexible spacers at equidistant points along the edge of the mold, then adding enough resin to fill the space between the mold and the lens placed over the mold, and supported by the flexible spacers. As an example, without any spacers, the thickness of the cured resin is found to be 0.07mm in Lens 2. With one type of flexible spacers, the thickness of the cured adhesive matrix layer increased to 0.16mm.

The formulation of Lens 1 is cured for 20 minutes, while the formulation of Lens 2 is cured for 25 minutes, both under ultraviolet radiation.

The stability of each of the adhesive matrix layers is tested as follows: the lenses with the attached adhesive matrix layers are immersed into reagent grade acetone at room temperature. It is found that coatings

1 and 2 remain bonded to the lens after 20 minutes. The lenses are then removed from the acetone bath and placed in a drying oven at 45°C overnight. Both lenses are clear, indicating that they are suitable for impregnation of additives which can be dissolved in acetone.

The adhesive matrix layers formed in Lens 1 and 2 are impregnated with photochromic additives dissolved to form a 2% by weight solution in acetone. The additives are dissolved to form a clear solution in acetone, then the lenses with the adhesive matrix superstrate layers are immersed into the solution, and left standing for periods ranging from 5 to 25 minutes at room temperature. It is found that both lenses (Lens 1 and 2), take up the additive in times as short as 5 minutes. Lens 1 adsorbs the additive faster than Lens 2. After a maximum of 25 minutes of immersion, the lenses are withdrawn from the solution, rinsed in acetone to remove surface deposits of the additive, then dried in a vacuum oven at or near room temperature (30°C-45°C) overnight.

The lenses are then overcast with an additional resin layer, to provide the add power correction and to provide the outer barrier layer, as described in Applicant's U.S. Patent Nos. 5,178,800, 5,147,585 and 5,219,497. In this process, a mold is selected so as to provide the add power correction of desired style and magnitude. The curvature of the mold has a precise relationship to the convex curvature of the lens with the adhesive matrix superstrate layer, so as to attain a preselected final convex curvature after the casting process is completed. Once the proper mold is selected, a specified volume of casting polymerizable resin specifically formulated to block as little UV light as possible is dispensed into the mold. Then the lens is simply allowed to settle on the resin mass, spreading it out into a uniform, thin layer on the distance portion of the mold and the lens, and a thicker layer on the add

portion of the mold. The mold assembly is then placed in a curing chamber, and the resin cured by the application of both UV radiation and heat. When the cure is complete, the mold assembly is allowed to cool slowly, and the lens is separated from the mold. The cured resin layer forms an optical quality front (convex) layer on the lens, effectively sandwiching the adhesive matrix layer between the new outer barrier layer and the lens body.

Example 2

A fixed volume of resin is placed in a mold whose curvature substantially matches the curvature of an optical substrate. After placing flexible spacers along the edge of the mold, the optical substrate is placed on the spacers so that the resin layer spreads out and fills the intervening space between the mold, optical substrate and spacers. The resin is then cured to form an optical substrate with an attached adhesive matrix layer. After demolding, the optical substrate and adhesive matrix layer are immersed in a solvent containing a photochromic additive. An outer barrier layer consisting of G-25, available from InnoTech, Inc., Roanoke, Virginia, is applied over the adhesive matrix layer in a thickness of greater than 50 μm, by means of a mold, followed by a photocuring step. Finally, an optional scratch-resistant coating can be applied, in this case on top of the outer barrier layer.

Example 3

An optical substrate is mounted on a rotating block, and a resin is sprayed on the optical substrate. The resin is then cured to form an optical substrate with an attached adhesive matrix layer. The optical substrate with an attached adhesive matrix layer is then sprayed with a solvent that contains a photochromic additive, followed by a drying step. The above

spraying, curing, spraying and drying steps are repeated 3-10 times to achieve an impregnated adhesive matrix layer with a thickness of 100-250 μm, followed by an annealing step to complete the cure and remove unreacted monomers. Finally, a hard coat which is significantly free of UV blocking and consisting of polyfunctional acrylates is applied over the adhesive matrix layer in a thickness of less than 25 μm, by spinning, followed by a photocuring step.

Example 4

An optical substrate is mounted on a fixture and placed in a resin bath whereupon photolithography is used to cure a 100-250 μm adhesive matrix layer on the optical substrate. The optical substrate with attached adhesive matrix layer is then removed from the resin bath, deblocked, and placed in a curing chamber to complete curing of the adhesive matrix layer. The adhesive matrix layer is then immersed in a solvent containing a photochromic additive. Finally, a hard coat which is significantly free of UV blocking and consisting of polyfunctional acrylates is applied over the adhesive matrix layer in a thickness of less than 25 μm, by dipping, followed by a photocuring step.

Example 5

An optical substrate is dipped in a resin bath, removed, and cured by applying a pulse of ultraviolet radiation. The resulting optical substrate with attached adhesive matrix layer is then sprayed with a solvent containing one or more photochromic additives, whereupon the solvent is flashed off. The above dipping, curing, spraying and flashing steps are preferably repeated 3-10 times to achieve an impregnated adhesive matrix layer having a cumulative thickness of 100-250 μm, followed by a post-cure step in a ultraviolet curing chamber to complete the cure and

remove unreacted monomers. Next, a hard coat which is significantly free of UV blocking and consisting of polyfunctional acrylates is applied over the adhesive matrix layer in a thickness of less than 25 μm, by spinning, followed by a photocuring step. Finally, the finished photochromic lens product is either aged or annealed to cause diffusion of the layered photochromic additives throughout the cumulative adhesive matrix layer.

Example 6

A specified volume of casting polymerizable resin is dispensed into a mold having an add power portion and a distance portion. A lens or semifinished blank having an attached adhesive photochromic matrix layer is allowed to settle on the resin mass, spreading it out into a uniform, thin layer on the distance portion of the mold, and a thicker layer on the add portion of the mold. The mold assembly is then placed in a curing chamber, and the resin cured by application of both ultraviolet radiation and heat. When the cure is complete, the mold assembly is allowed to cool slowly, and the lens is separated from the mold. The cured resin layer forms an optical quality outer barrier layer on the front (anterior surface) of the lens, effectively sandwiching the adhesive photochromic matrix layer between the new outer barrier layer and the lens body.

CLAIMS

1. An optical product comprising an adhesive matrix layer attached to an optical substrate and having a thickness of greater than 25 μm, said adhesive matrix layer containing one or more photochromic additives.

2. The optical product of claim 1, further comprising an outer barrier layer attached to said adhesive matrix layer, said outer barrier layer being substantially impermeable to said one or more photochromic additives.

3. An optical product comprising: an adhesive photochromic matrix layer attached to an optical substrate; and an outer barrier layer attached to said adhesive photochromic matrix layer, said outer barrier layer being attached without the use of an additional adhesive.

4. The optical product of claim 1, wherein said adhesive photochromic matrix layer is provided on a surface of said optical substrate selected from the group consisting of a convex surface of said optical substrate, a concave surface of said optical substrate, and both convex and concave surfaces of said optical substrate.

5. The optical product of claim 1, wherein said optical substrate is selected from the group consisting of an optical preform, an optical window, an optical wafer, an optical lens, and a semi-finished lens blank.

6. The optical product of claim 1, wherein said adhesive matrix layer has a refractive index that is within 0.05 refractive index units of the refractive index of said substrate.

7. The optical product of claim 1, wherein said adhesive matrix layer is resistant to solvents selected from the group consisting of organic solvents, silicone oils, fluorinated silicone oils, and fluorocarbons.

8. The optical product of claim 1, wherein said outer barrier layer is a scratch resistant layer.

9. The optical product of claim 1, wherein said outer barrier layer has a T_g of more than about 70°C.

10. The optical product of claim 1, wherein said adhesive matrix layer has a cross link density that is less than that of commercially available CR-39 lenses.

11. The optical product of claim 1, wherein said adhesive matrix layer has a Tg between 10 and 60 °C.

12. The optical product of claim 1, wherein said one or more photochromic additives are selected from the group consisting of spiro(indolino) naphthoxazines, spiro(indolino) pyridobenzoxazines, spiro(benzindolino) naphthoxazines, and spiro(benzindolino) pyridobenzoxazines.

13. The optical product of claim 1, wherein said adhesive matrix layer comprises at least two adhesive matrix sublayers.

14. The optical product of claim 13, wherein said each of said at least two adhesive matrix sublayers contains a different photochromic additive.

15. An adhesive matrix layer having a thickness of greater than 25 μm that is adapted to act as a reservoir for one or more photochromic additives and as a transition region between dissimilar materials, said

adhesive matrix layer having one or more characteristics selected from the group consisting of a cross link density that is less than that of commercially available CR-39 lenses and a Tg between 10 and 60 °C.

16. The adhesive matrix layer of claim 15, wherein said one or more photochromic additives are selected from the group consisting of spiro(indolino) naphthoxazines, spiro(indolino) pyridobenzoxazines, spiro(benzindolino) naphthoxazines, and spiro(benzindolino) pyridobenzoxazines.

17. A method for the manufacture of an optical substrate having an attached adhesive matrix layer comprising:

providing an optical substrate; and providing an adhesive matrix layer having a thickness greater than 25 μm on at least one surface of said optical substrate, said adhesive matrix layer containing one or more photochromic additives.

18. The method for the manufacture of an optical substrate having an attached adhesive matrix layer of claim 17, comprising the steps of:

providing a mold;

coating said mold with an adhesive matrix resin corresponding to said adhesive matrix layer, to form a coated mold;

providing an accessory mold and a substrate resin; arranging said coated mold, said accessory mold and said substrate resin such that the space between said coated mold and said accessory mold is filled with said substrate resin and such that the volume occupied by said substrate resin corresponds to the shape of the optical substrate; and

curing said substrate resin.

19. The method of claim 18, wherein said mold is provided with a resin corresponding to a hard coat material prior to coating said mold with said adhesive matrix resin.

20. The method of claim 18, wherein a photochromic additive is provided within said adhesive matrix resin prior to curing.

21. The method of claim 18, wherein a photochromic additive is provided within said adhesive matrix layer after curing.

22. The method of claim 18, further comprising placing a photochromic layer on the mold prior to coating the mold with said adhesive matrix resin.

23. The method of claim 19, wherein a photochromic layer is placed in the resin corresponding to said hard coat material prior to coating the mold with said adhesive matrix resin.

24. The method for the manufacture of an optical substrate having an attached adhesive matrix layer of claim 17, comprising the steps of: providing said optical substrate; providing an adhesive matrix resin on at least one surface of said substrate; and curing said adhesive matrix resin to form said adhesive matrix layer.

25. The method of claim 17, wherein said adhesive matrix resin is provided on said at least one surface of said substrate by means of a mold.

26. The method of claim 17, wherein said adhesive matrix resin is provided on said at least one surface of said substrate by an application step selected from the

group consisting of dip coating, brushing, dripping, spraying, flow coating, photolithography and spin coating said optical substrate.

27. The method of claim 26, wherein said adhesive matrix resin is cured either concurrently with or subsequent to said application step.

28. The method of claim 17, further comprising the steps of: providing said optical substrate; immersing said optical substrate in an adhesive matrix resin bath; and curing said adhesive matrix resin on said optical substrate, while said optical substrate is immersed in said adhesive matrix resin.

29. The method of claim 17, wherein one or more photochromic additives selected from the group consisting of spiro(indolino) naphthoxazines, spiro(indolino) pyridobenzoxazines, spiro(benzindolino) naphthoxazines, and spiro(benzindolino) pyridobenzoxazines is incorporated into said adhesive matrix layer.

30. The method of claim 29, wherein said additive is incorporated into said adhesive matrix layer from a solvent solution containing said one or more photochromic additives using a method selected from the group consisting of immersing, brushing, dripping, spraying, flow coating and spin coating, followed by removal of residual solvent.

31. The method of claim 30, wherein said solvent is selected from one or more solvents from the group consisting of organic solvents, silicone oils, and fluorinated oils.

32. The method of claim 17, further comprising providing an outer barrier layer on said adhesive matrix layer.

33. The method of claim 17, wherein said adhesive matrix layer is subjected to one or more dispersion processes selected from the group consisting of ageing, annealing, vibration, ultraviolet radiation and infrared radiation to further disperse said one or more photochromic additives within said adhesive matrix layer.

34. A method for the manufacture of an optical substrate having an attached adhesive matrix layer comprising:

(a) providing said optical substrate;

(b) providing a first adhesive matrix sublayer on at least one surface of said substrate; and

(c) providing a second adhesive matrix sublayer on said first adhesive matrix sublayer to provide a network of adhesive matrix sublayers.

35. The method of claim 34, wherein step (d) is repeated at least once.

36. The method of claim 34, wherein said network of adhesive matrix sublayers is provided with one or more photochromic additives.

37. The method of claim 36, wherein one or more first photochromic additives are incorporated into said first adhesive matrix sublayer after step (b) and one or more second photochromic additives are incorporated into said first adhesive matrix sublayer after step (c).

38. The method of claim 37, wherein said one or more first photochromic additives differ from said one or more second photochromic additives.

39. The method of claim 37, wherein said one or more first photochromic additives are the same as said one or more second photochromic additives.

40. The method of claim 36, wherein said network of adhesive matrix sublayers is provided with one or more photochromic additives in a single step.

41. The method of claim 34, further comprising providing an outer barrier layer on said adhesive matrix layer.

42. The method of claim 41, wherein said outer barrier layer is a layer selected from the group consisting of a scratch resistant resin, an anti-reflective resin, a resin that is resistant to permeation by said photochromic additives, and a resin that is resistant to permeation by oxygen.

43. The method of claim 41, wherein said outer barrier layer is provided from a method selected from the group consisting of molding, in-mold coating transfer, brushing, dripping, spraying, flow coating, photolithography, and spin coating a resin corresponding to said outer barrier layer on said adhesive matrix layer.

44. The method of claim 41, wherein said outer barrier layer includes an add power zone.

45. The method of claim 41, wherein said adhesive matrix layer and said outer barrier layer are further coated with an outermost hard coat layer.

46. The method of claim 36, wherein said first and second adhesive matrix sublayers are subjected to one or more dispersion processes selected from the group consisting of ageing, annealing, vibration, ultraviolet radiation and infrared radiation to further disperse said one or more photochromic additives within said adhesive matrix layer.

47. The method of claim 46, wherein said adhesive matrix sublayers are subjected to said one or more dispersion processes prior to a step of curing said adhesive matrix sublayers.

48. The method of claim 46, wherein said adhesive matrix sublayers are subjected to said one or more dispersion processes during a step of curing said adhesive matrix sublayers.

49. The method of claim 46, wherein said adhesive matrix sublayers are subjected to said one or more dispersion processes after a step of curing said adhesive matrix sublayers.

50. The method of claim 17, wherein said adhesive matrix layer has one or more characteristics selected from the group consisting of a cross link density that is less than that of commercially available CR-39 lenses and a Tg between 10 and 60°C.

51. The method of claim 24, further comprising placing a layer of photochromic material on said optical substrate prior to providing said adhesive matrix resin.

52. The method of claim 34, further comprising placing a layer of photochromic material on said optical substrate prior to providing said first adhesive matrix sublayer.

53. The optical product of claim 1, further comprising a layer of photochromic material between said optical substrate and said adhesive matrix layer.

54. The optical product of claim 3, further comprising a layer of photochromic material between said optical substrate and said adhesive matrix layer.

55. The optical product of claim 1, wherein said adhesive matrix layer is subjected to one or more dispersion processes selected from the group consisting of ageing, annealing, vibration, ultraviolet radiation and infrared radiation to further disperse said photochromic additives within said adhesive matrix layer.

56. The optical product of claim 3, wherein said adhesive matrix layer is subjected to one or more dispersion processes selected from the group consisting of ageing, annealing, vibration, ultraviolet radiation and infrared radiation to further disperse said photochromic additives within said adhesive matrix layer.

57. The adhesive matrix layer of claim 15, wherein said adhesive matrix layer is subjected to one or more dispersion processes selected from the group consisting of ageing, annealing, vibration, ultraviolet radiation and infrared radiation to further disperse said photochromic additives within said adhesive matrix layer.

58. The optical product of claim 1, wherein the photochromic additives are provided in a form selected from the group of: a mechanical mixture of various components, a co-precipitated form of the various

additives, and microencapsulated within a layer of thermoplastic polymer.

59. The optical product of claim 3, wherein the photochromic additives are provided in a form selected from the group of: a mechanical mixture of various components, a co-precipitated form of the various additives, and microencapsulated within a layer of thermoplastic polymer.

60. The adhesive matrix layer of claim 15, wherein the photochromic additives are provided in a form selected from the group of: a mechanical mixture of various components, a co-precipitated form of the various additives, and microencapsulated within a layer of thermoplastic polymer.

61. The method of claim 17, wherein the photochromic additives are provided in a form selected from the group of: a mechanical mixture of various components, a co-precipitated form of the various additives, and microencapsulated within a layer of thermoplastic polymer.

62. The method of claim 36, wherein the photochromic additives are provided in a form selected from the group of: a mechanical mixture of various components, a co-precipitated form of the various additives, and microencapsulated within a layer of thermoplastic polymer.

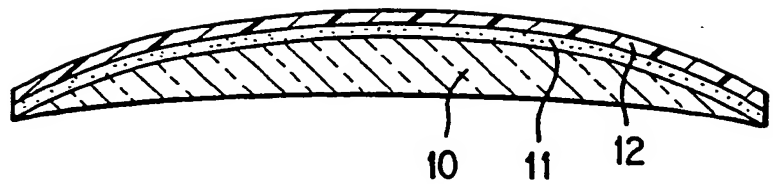

FIG.1

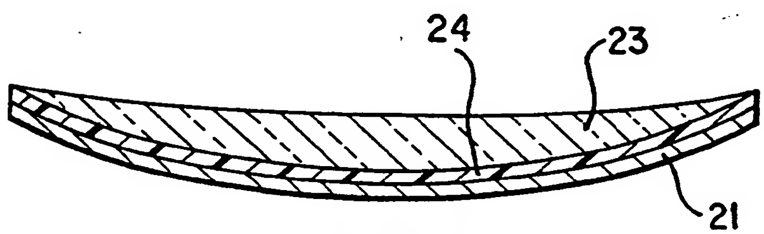

FIG. 2A

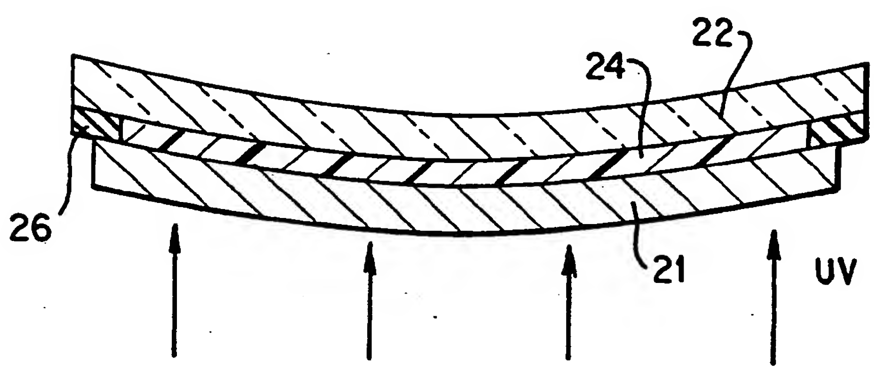

FIG. 2B

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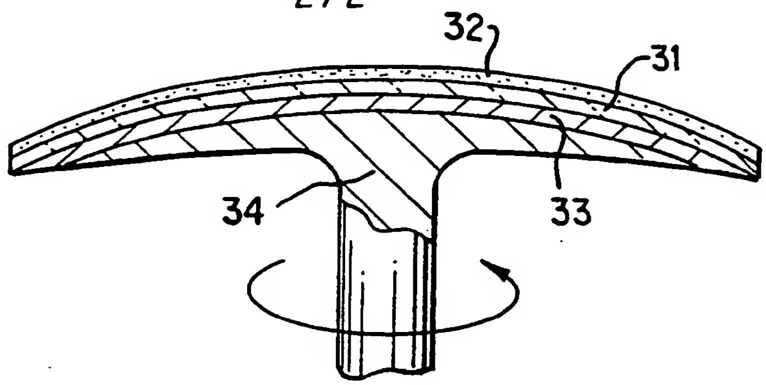

FIG. 3

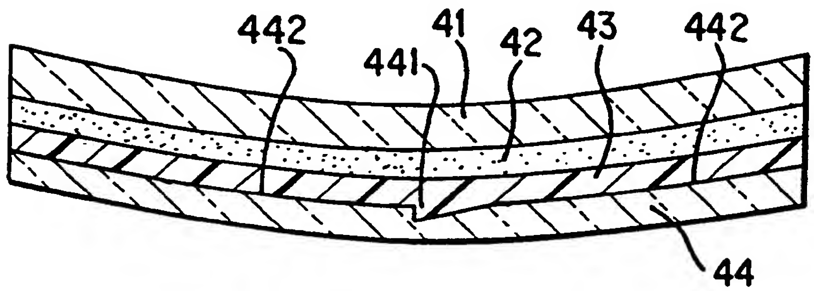

FIG. 4

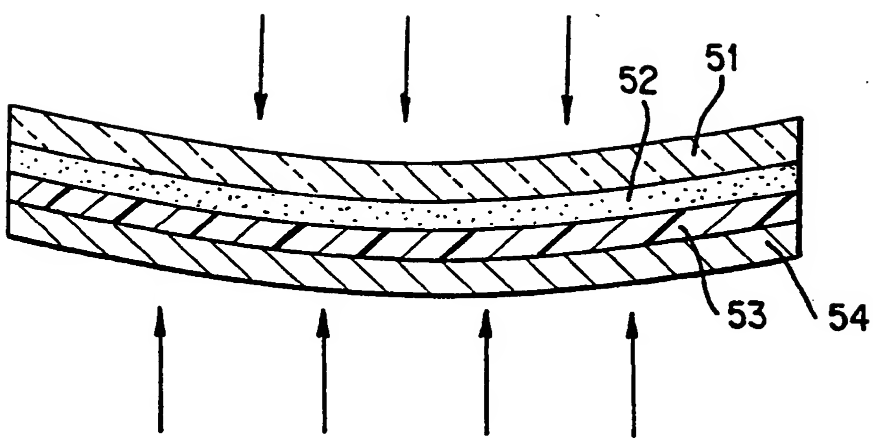

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/06348

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B29D 11/00
US CL :351/165; 264/1.7
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 351/159, 165, 166, 177; 264/1.7; 252/386; 425/810; 428/343

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,219,497 (BLUM ET AL) 15 JUNE 1993, SEE WHOLE DOCUMENT	1-62
Y	US, A, 5,180,524 (CASILLI ET AL) 19 JANUARY 1993, SEE WHOLE DOCUMENT	12, 16, 29
Y	US, A, 4,936,995 (KWIATKOWSKI) 26 JUNE 1990, SEE WHOLE DOCUMENT	12, 16, 29

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 JULY 1996	08 AUG 1996

Name and mailing address of the ISA/US	Authorized officer
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